ORIGIN OF THE SUNSPOT MODULATION OF OZONE: ITS IMPLICATIONS FOR STRATOSPHERIC NO INJECTION

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The measured modulation of cosmic rays deposited in the stratosphere over a sunspot cycle produces an oscillating source of stratospheric NO with an 11-year (quasi) period. The resulting modulation of ozone over this period is calculated and is shown to give good agreement with available measurements of the time lag, the latitude dependence, and the magnitude of cyclic variations of ozone. This correlated modulation is then used to predict the effect on ozone of the injection

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19. KEY WORDS (Continued)

20 ABSTRACT (Continued)

of NO into the stratosphere from artificial sources, viz., a fleet of supersonic transports and nuclear bomb explosions in the atmosphere.

CONTENTS

ILLUSTRATIONS

I INTRODUCTION

That cosmic-ray ionization is a source for NO_x in the stratosphere was noted by Warneck.[1]* He and, to a more extensive degree, Brasseur and Nicolet,[2] examined the worldwide contribution of this NO_x source compared with other sources, and it appears to be relatively minor. Hence, the catalytic destruction of ozone by cosmic-ray-induced NO_x presumably plays a small role in determining stratospheric ozone abundances. But because of varying solar magnetic-field effects during the (~11-yr) sunspot cycles, low-energy cosmic rays incident upon the higher ($\geq 60°$) latitude regions of the earth's atmosphere are modulated with the sunspot (quasi) period. The 11-year variation in stratospheric ionization has been measured for many years. The ionization produces N and N^+; these in turn react to produce predictable amounts of NO_x. The abundances and temperatures in the stratosphere, together with measured reaction rates, imply that essentially all of these free N atoms and ions ultimately result in the formation of NO. Thus there is an oscillating source of NO of known strength and spatial distribution in the stratosphere at the high latitudes of both hemispheres. If NO has the expected qualitative effect on ozone abundance, some cyclic variation in stratospheric ozone should exist with essentially the periodicity of the sunspot cycle (or more precisely that of the modulation of low-energy cosmic-ray flux associated with it). We show below in Section IV that, at those two ozone measuring stations (Tromso and Arosa) where published records extend back 40 years, the measured, integrated ozone-column densities not

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*References are listed at the end of the report.

only appear to have the expected periodicity but also show the calculated phase lag relative to the sunspot cycle. Worldwide data, available after the mid-1950's, show a dependence of this correlation on latitude, and the time lag and relative amplitude at different stations are in reasonable agreement with the calculated ones. The absolute magnitude of the periodic ozone modulation is also shown to be consistent with that expected from typical models for the stratosphere, wherein NO plays a major role in controlling the ozone abundance. These various coincidences between the observed and calculated quasi-periodic modulations of ozone abundance suggest that the known variation of stratospheric NO injection produces the measured variations of ozone. Having established that the ozone variability is roughly proportional (with some time delay) to the change in NO density, then the effect of known NO injection into the same regions of the stratosphere by SST aircraft (or nuclear explosions) is calculable (Section 7).

II SUNSPOT-CYCLE MODULATION OF STRATOSPHERIC COSMIC-RAY IONIZATION

The formation of ion pairs by cosmic rays has been studied at high latitudes as a function of altitude over three sunspot cycles.[3,4] Results are summarized in Figures 1 through 4. It is clear that ionization deposited at stratospheric heights is strongest over the polar caps, where the magnetic field is weakest, and that a sharp drop occurs below 60° geomagnetic latitude. The peak ion production is between 11 and 15 km above the Arctic tropopause at 8 to 9 km. The mean peak is about 35 ion-pair cm s, with an amplitude through the sunspot cycle of about ±15 percent. The total ionization in a column averages about 4.5×10^7 ion-pair cm^{-3} s^{-1}, with an amplitude through the sunspot cycle of about ±15 percent. The total ionization in a column averages about 4.5×10^7 ion-pair cm^{-2} s^{-1}.

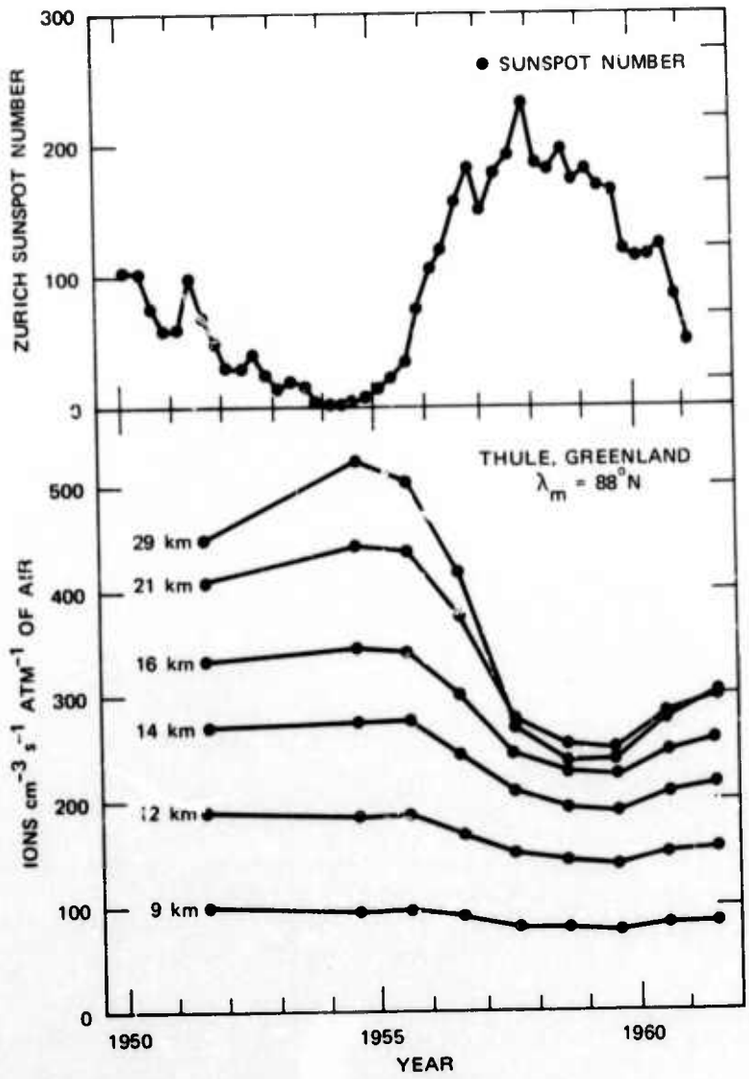

FIGURE 1 CORRELATION OF SUNSPOT NUMBER WITH IONIZATION AT SELECTED PRESSURES OVER THULE, GREENLAND.[3] The pressures are specified by equivalent altitude in a Standard Model Atmosphere. (The ionization must be multiplied by the pressure in atmospheres to find ion pairs cm^{-3}.)

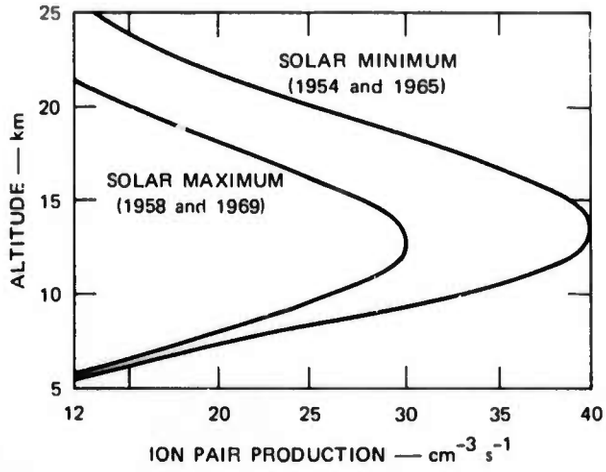

FIGURE 2 VARIATION OF COSMIC-RAY-INDUCED ATMOSPHERIC IONIZATION IN THE ATMOSPHERE OVER THULE, GREENLAND, BETWEEN SUNSPOT MAXIMUM AND MINIMUM. Source: Ref. 2, from data of Ref. 4.

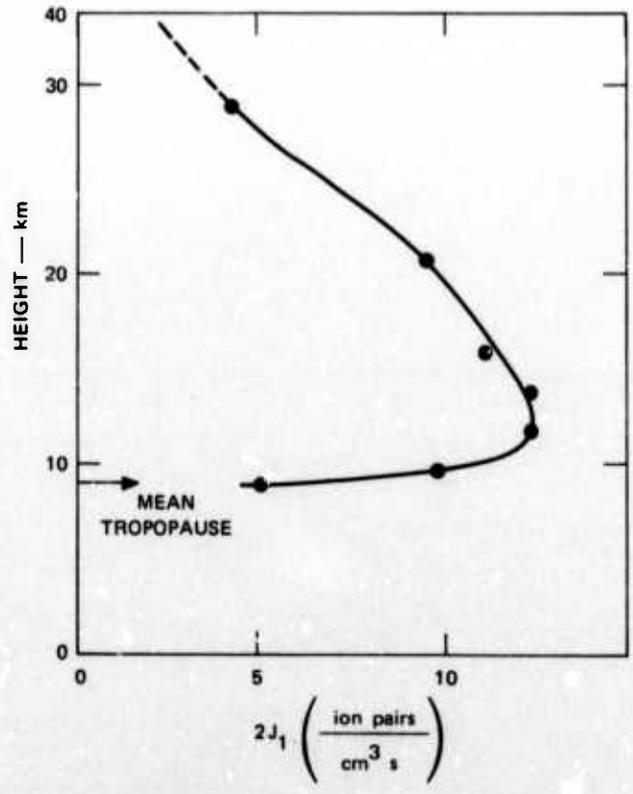

FIGURE 3 AMPLITUDE OF OSCILLATING COMPONENT OF STRATOSPHERIC IONIZATION FOR THE DATA OF FIGURE 1 AND THE STANDARD MODEL ATMOSPHERE AS A FUNCTION OF ALTITUDE (km). The abscissa is the maximum ionization variation $2I_1$; the ionization $I = I_0 + I_1 \cos \omega t$ in ion pairs cm^{-3} s^{-1}.

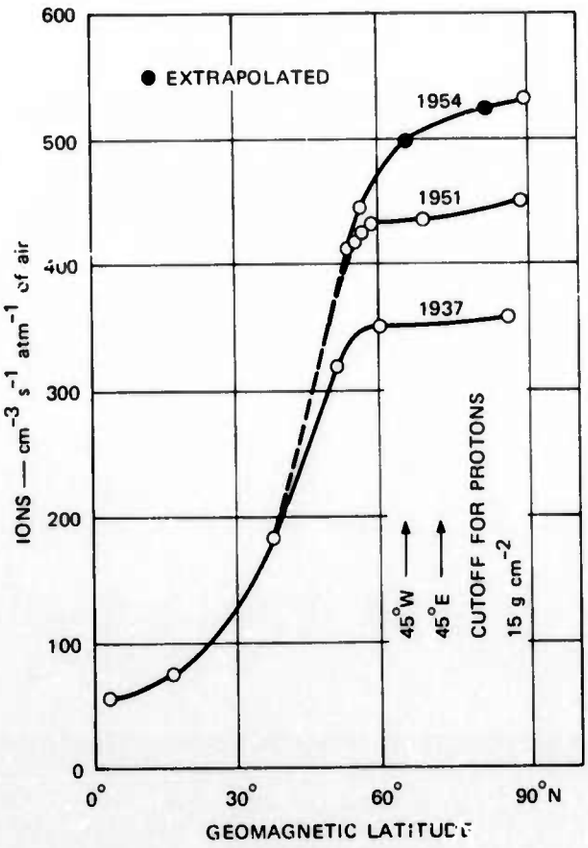

FIGURE 4 IONIZATION vs. LATITUDE FOR CONSTANT OVERHEAD AIR MASS OF 15 g cm^{-2} FOR THREE DIFFERENT YEARS. In 1937 the sun was at a maximum of activity while in 1954 it was at a minimum. The pressure of 15 g cm^{-2} corresponds to about 30 km altitude. The vertical arrows show the latitudes, at two zenith angles, for cutoff by the geomagnetic field of primary cosmic rays that can just penetrate an air mass of 15 g cm^{-2}. Source: Ref. 5.

III MODULATED NO INJECTION BY COSMIC RAYS

Calculations by Dalgarno[6] on the distribution of collision products from ionizing particles in air were used by Warneck[1] to estimate that 0.33 NO molecule is produced for each ion pair. However, Brasseur and Nicolet[2] argue that the dissociation of N_2 by secondary-electron impact should be increased by a factor of three, and the NO production should be raised by about the same factor. More detailed calculations by Gilmore[7] give a yield of 1.3 N atoms per ion pair.

This is also effectively the rate of production of NO per ion pair produced by cosmic rays via reaction (2) below. In a note added in proof, Warneck mentions that N can also destroy NO. Indeed, the reaction

$$N + NO \rightarrow N_2 + O \qquad (1)$$

has one of the fastest two-body rate coefficients known.[8,9] The rate has been measured as about 2×10^{-11} cm^3 s^{-1} at 300° K and it varies as 5×10^{-11} exp (-100/T) at somewhat higher temperatures (475° to 750° K). Hence we adopt

$$k_1 = 2.8 \times 10^{-11} \exp(-100/T) \text{ cm}^3 \text{ s}^{-1}$$

for stratospheric temperatures.

The NO creation mechanism is

$$N + O_2 \rightarrow NO + O \quad . \qquad (2)$$

Vlastraras and Winkler,[10] and Wilson[11] give formulae yielding results that differ by a factor of two when extrapolated to the 200° K regime. The Vlastraras-Winkler coefficient, which gives the larger values, is

$$k_2 = 6.5 \times 10^{-12} \exp(-3500/T) \text{ cm}^3 \text{ s}^{-1} \quad .$$

Figure 5 gives [NO] fractional concentrations for three different formulae for the rate coefficient, k_2, when N and NO are in chemical equilibrium through reactions (1) and (2). In the lower stratosphere, where the pressure is 0.1 atm, the density is $[M] = 2 \times 10^{-18}$ cm^{-3} and T = 220° K, the equilibrium concentration [NO]/[M], exceeds 4×10^{-9}. The equilibrium mole fractions of NO in the presence of a continued injection of N atoms are plotted versus altitude in the Standard Model Atmosphere[12] in Figure 6. The actual relative concentration of stratospheric NO in a steady state is not well known. While theoretical models suggest chemical-equilibrium concentrations exceeding 10^{-9}, measurements around 21 km by Ridley et al.[13] give only about 10^{-10}. However, spectroscopic measurements by Toth et al.[14] from aircraft indicate concentrations of 10^{-9} in the altitude range 11 to 26 km. Even if the equilibrium NO abundance for thermalized chemistry were achieved, N atoms produced from cosmic-ray ionization would still make NO more rapidly than it would destroy it. Gilmore[7] finds that more than half of the N atoms are created in the metastable states ^{2}D(2.37 eV) or ^{2}P(3.56 eV), which are not readily quenched by thermal collisions with N_2 molecules. With this energy available to counteract the large activation energy of reaction (2), the rate coefficient k_2 could be increased[15,16] by a factor of 10^5. (In addition, the initial kinetic energy of the N atoms will likely exceed the local thermal energies and remain so for the first few collisions with N_2 molecules.) Thus, more than half the N atoms are expected to

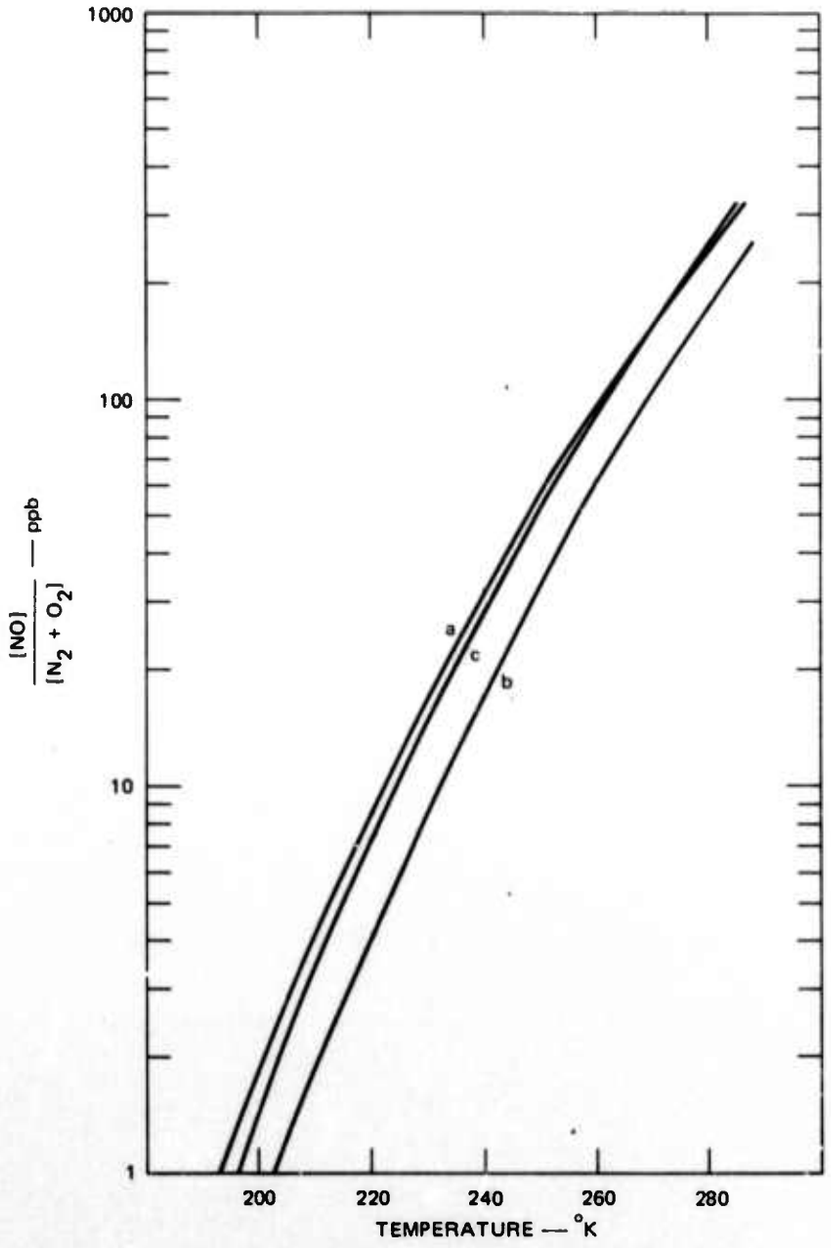

FIGURE 5 PARTIAL MOLE FRACTION OF NO IN PARTS PER BILLION (10^{-9}) VERSUS TEMPERATURE AT WHICH THE NET RATE FOR PRODUCTION OF NO BY N VANISHES — i.e., $N + NO \rightarrow N_2 + O = N + O_2 \rightarrow NO + O$, WHERE N IS ASSUMED TO BE THERMALIZED IN THE GROUND STATE. The three curves represent three extrapolations from measurements at higher temperatures (cf. Section III): $k_{2a} = 6.5 \times 10^{-12} \exp(-3500/T)$, source: Ref. 10; $k_{2b} = 2.33 \times 10^{-11} \exp(-3950/T)$, source: Ref. 11; $k_{2c} = 4.98 \times 10^{-13} T^{1/2} \exp(-3565/T)$, source: Ref. 11.

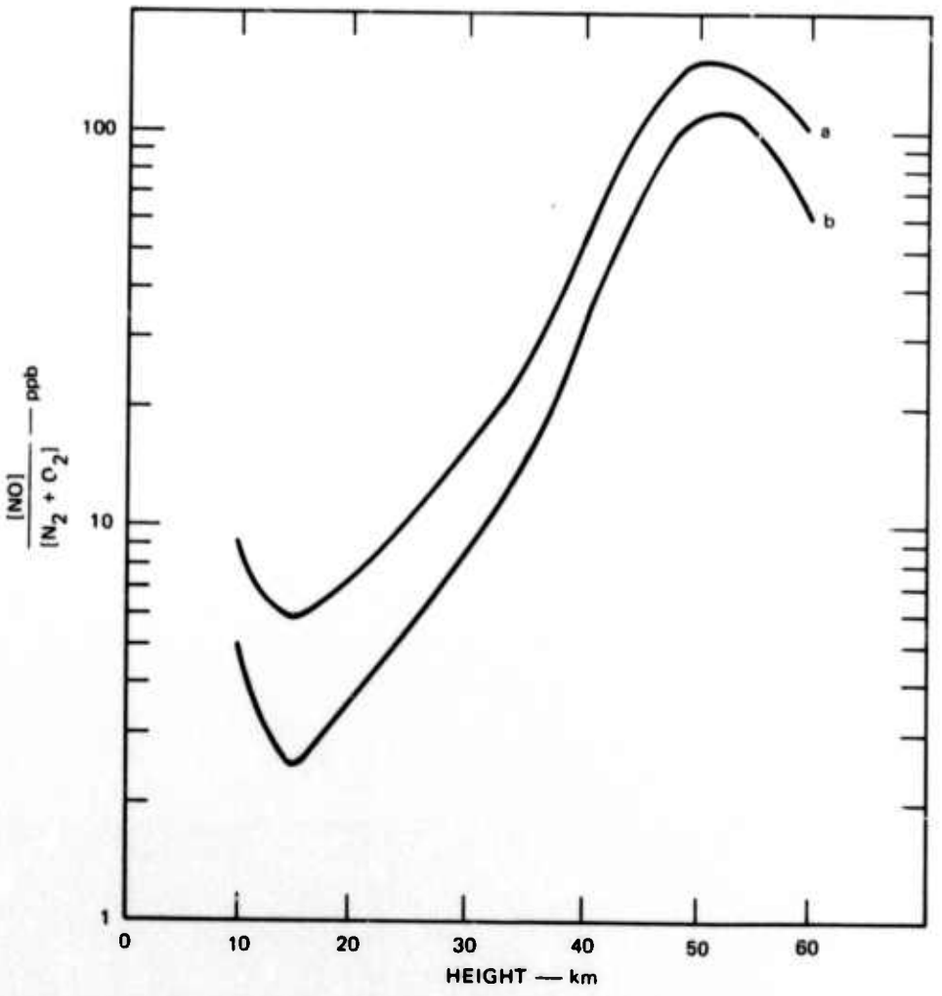

FIGURE 6 PARTIAL MOLE FRACTION OF NO IN PARTS PER BILLION FOR WHICH THERMALIZED GROUND STATE N ATOMS WOULD PRODUCE NO NET NO IN A STANDARD MODEL ATMOSPHERE. The maximum and minimum rate coefficients of Figure 5 are used.

make NO through reaction (2) no matter how high the NO fractional abundance. In our numerical estimates we shall assume all do.

Throughout the above discussion we have supposed for definiteness that NO_x is entirely in the form NO. However, if it were largely NO_2, as it may be in the lower stratosphere, our conclusion that N mainly manufactures NO_x, instead of destroying it, is unchanged. The rate coefficient for $N + NO_2$ reactions at 300° K is also large,[17] about 1.8×10^{-11} cm^3 s^{-1}. However, there are four possible end products and the creation of 2 NO's has a 1/3 branching ratio. Hence the destruction of NO_x is down by a factor of about 3, when the reactant is NO_2, compared with the loss rate of NO by reaction (1). Consequently, any NO_2 present will have the net effect of increasing the NO_x caused by cosmic-ray-produced N.

IV EVIDENCE FOR THE CORRELATION OF OZONE WITH THE SOLAR CYCLE

Claims for the existence of a correlation of ozone abundance with sunspot activity have an extensive history. Recent analyses of 30-month running averages of ozone column densities by Angell and Korshover[18] seem to offer significant support for such a correlation. Their processed data are given in Figures 7 and 8. Only two stations, Tromso and Arosa, are given with data extending back far enough to cover several sunspot cycles. Both stations appear to have very significant correlation with solar magnetic activity. For the sunspot cycle around 1960, after the extensive worldwide ozone data collection of the mid-1950's began, hemispheric and equatorial ozone also seem to correlate with sunspots but with smaller amplitude. (The 30-month running average Northern Hemisphere data seem to be irregular in the interval around 1960; this appears not only in the extensive data of Figure 8 but apparently also in the more erratic ozone data from Arosa and Tromso. An effect on the 30-month averaging of the extensive Arctic nuclear-explosion program beginning mid-1961 might be expected from some ozone suppression by bomb-injected NO. If so, the data suggest the averaged effect may be of the order 1/2 percent for the Northern Hemisphere. During this particular sunspot cycle, Northern Hemisphere correlation data may be suspect.) If the correlation exists, the effect is strongest near the poles (Tromso, 70°) where the ozone maximum typically lags the sunspot maximum by two to three years; it is progressively weaker and has a greater time lag at lower latitudes. Just this qualitative behavior would be expected from cyclical injection at high latitudes of some catalyst which destroys ozone (or enhances it--depending on the phase relation of catalyst

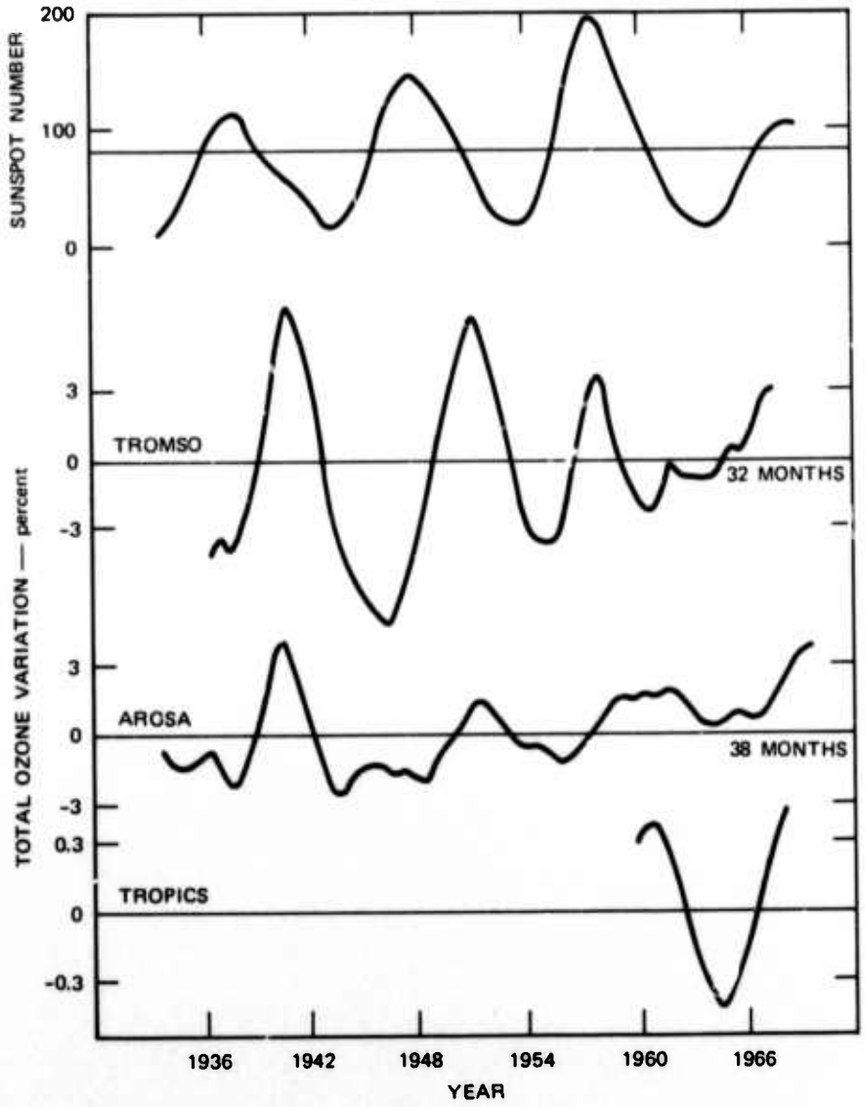

FIGURE 7 COMPARISON OF TEMPORAL VARIATION IN SUNSPOT NUMBER (top) WITH THE PERCENTAGE DEVIATION FROM THE MEAN OF THE 30-MONTH RUNNING AVERAGES OF TOTAL OZONE. The data for the tropics are "smoothed" and have a scale one-tenth that of Arosa (47°N) and Tromso (70°N). For Tromso and Arosa, for which over 30 years data are available, the average phase lag of ozone variation relative to that of sunspot count is given in months. Source: Ref. 18.

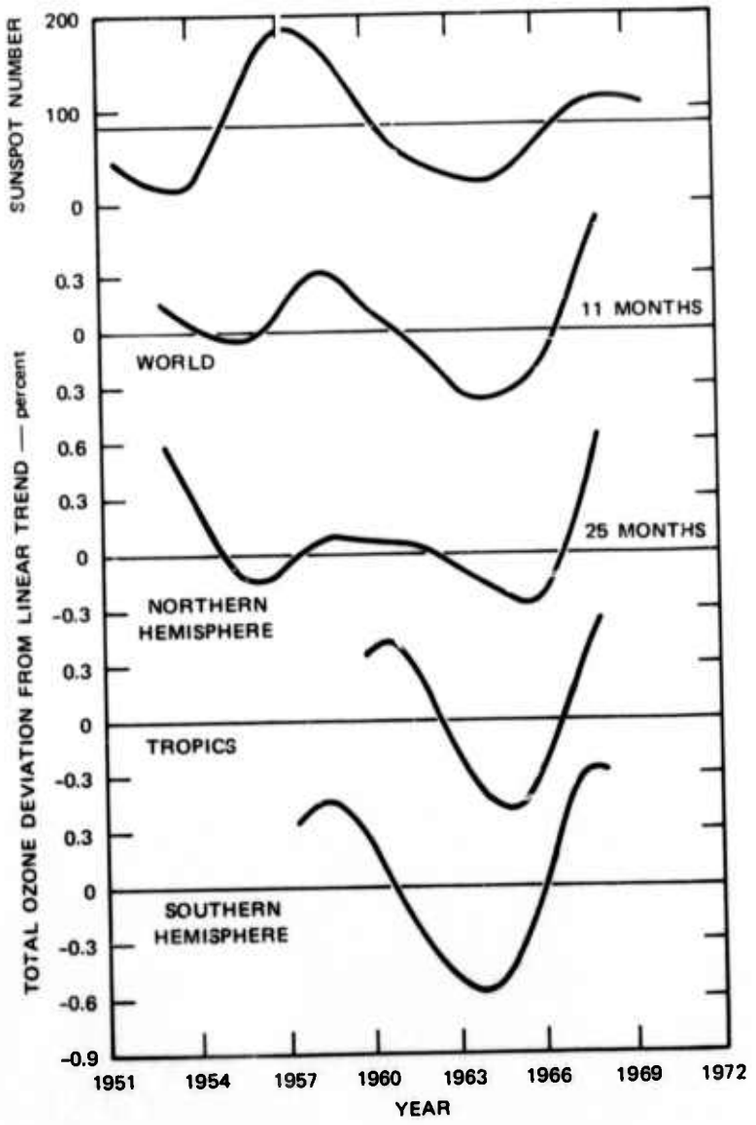

FIGURE 8 COMPARISON OF THE TEMPORAL VARIATION IN SUNSPOT NUMBER WITH THE SMOOTHED PERCENTAGE DEVIATION FROM THE LINEAR TREND OF 30-MONTH RUNNING AVERAGES OF TOTAL OZONE. Fits for the lag in response of the world zone and the Northern Hemisphere zone relative to the sunspot variation are given at right. Source: Ref. 18.

injection with sunspot cycle): the relative time lag and the amplitude decrease with increasing distance from the poles are characteristic of eddy diffusion away from an oscillating polar source. In the next sections we show how the observations are more quantitatively consistent with the model calculations. If the solar cycle were to modulate stratospheric ozone by altering solar radiation in an appropriate part of the ultraviolet spectrum, its initial effect on the earth would probably be worldwide and simultaneous, thereby giving a temporal and spatial pattern to resulting ozone variations very different from that found by Angell and Korshover [18]

V CALCULATED TIME DELAYS AND RELATIVE AMPLITUDES FOR MODULATED OZONE AT VARIOUS LATITUDES

We consider an idealization of the stratosphere in which the residence time τ for NO is (cf. Figure 9)

$$\tau \sim 2 \text{ to } 6 \text{ years} \tag{3}$$

and in which horizontal diffusion is described by a conventional constant horizontal eddy-diffusion coefficient,

$$K \sim 5 \times 10^{9} \text{ cm}^{2} \text{ s}^{-1} \quad . \tag{4}$$

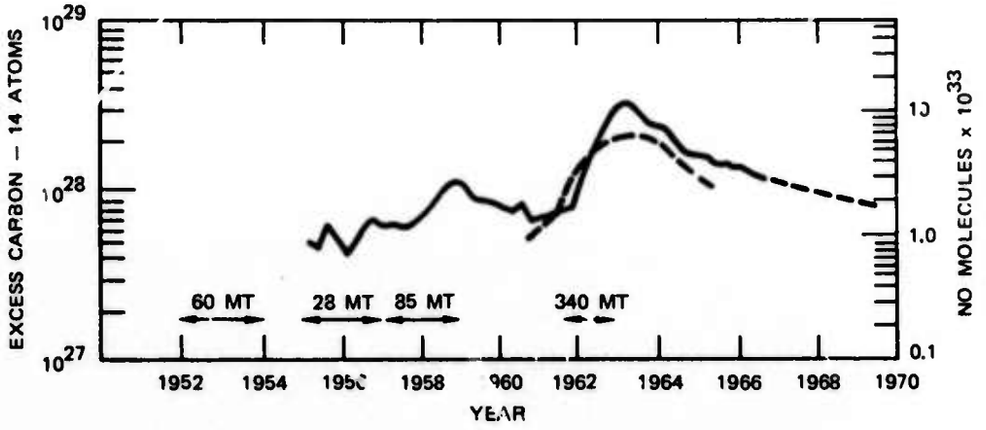

FIGURE 9 "MEASURED" STRATOSPHERIC BURDEN OF BOMB MANUFACTURED C^{14}. Source: Refs. 19 and 20. The left scale is that for C^{14}. The right is for NO on the assumption that a one megaton air explosion which locally forms 2×10^{26} C^{14} atoms (Ref. 21) also forms 4×10^{31} NO atoms. The latter is the lower bound of Gilmore (Ref. 7) and almost that of Ref. 22. The solid line is the total stratospheric burden; the dashed line is the 30-month running average for the Northern Hemisphere alone. Bomb yields are given in megatons for testing intervals.

Then in the presence of an NO source J, we have

$$\frac{d}{dt}[NO] = J - \frac{[NO]}{\tau} + K\nabla_2^2[NO] \quad , \tag{5}$$

where ∇_2^2 is the two-dimensional Laplacian over the surface of the terrestrial sphere. We assume the source has an oscillating component

$$J = J_o + J_1 e^{i\omega t} \tag{6}$$

with

$$\omega \simeq \frac{2\pi}{11 \text{ years}} \quad . \tag{7}$$

The amplitude J_1 is constant in the high latitude regions, $\theta \geq \theta_o \sim 60^\circ$, and is zero away from the polar regions where $\theta < \theta_o$. Equations (5) and (6) are easily solved in terms of the Legendre functions P_ν (cos θ) and Q_ν (cos θ) but with complex ν. The analogous solution on an infinite plane with uniform oscillating injection within a circle of radius r_o is developed in Appendix A. For the special case

$$\left(\omega^2 + \tau^{-2}\right)^{1/2} \frac{r_o^2}{4K} \ll 1 \tag{8}$$

this solution becomes [Eq. (A-20)]

$$[NO] \sim \frac{0.4\ J_1 r_o^2}{K} \exp\left[i\omega(t - \Delta)\right] \tag{9}$$

for $r < r_o$ with the time lag Δ. For the parameters of Eqs. (3), (4), and (7), we obtain

$$\Delta \sim 1.3 \text{ years} \quad . \tag{10}$$

(If $K = 0$, or $K = \infty$ on a sphere, then the solution becomes $\Delta = \omega^{-1} \tan^{-1} \omega\tau = 1.8$ years for $\tau = 3$ years.) For the polar-cap region over which the cosmic-ray solar-cycle variation is strong--i.e., for latitudes above 60°--we obtain

$$r_o \sim \Phi_o R_e \sim 3 \times 10^8 \text{ cm} \quad , \tag{11}$$

with R_e the earth radius and Φ_o the colatitude in radians (= 30/57.3). Then the left-hand side of Eq. (8) is 1/10, supporting the approximation. For distances beyond r_o, corresponding to latitudes below $\theta_o = 60°$, we make the association $r = R_e\varphi$, with $\varphi = (\pi/2 - \theta)$ the colatitude in radians. Then for $\tau \sim 3$ years, we find

$$[NO] = [NO]_o \left(\frac{\varphi_o}{\varphi}\right)^{1/2} \exp\left\{-\left(\varphi - \varphi_o\right)(1.1 + 0.62\ i)\right\} \quad , \quad \theta < \theta_o \tag{12}$$

where $[NO]_o$ is the density at $\theta = \theta_o$, given by Eq. (A-20).

The observed time lag between sunspot maximum and NO minimum is, on this model, the sum of three lags:

$$t_L = t_I + \Delta + \delta_\theta \quad , \tag{13}$$

with Δ the lag of Eq. (10) characterizing the oscillation of [NO] over the polar cap, δ_θ the additional latitude-dependent lag of Eq. (12), and t_I the lag between sunspot maximum and cosmic-ray ionization minimum. Balloon measurements (Neher and Anderson,[3] and Neher,[4,5]) give

$$t_I \sim 0.8 \text{ to } 1.0 \text{ years} \quad . \tag{14}$$

Therefore, for Tromso ($\theta = 70°$), assuming $t_I = 1$ year,

$$t_L \text{ (Tromso)} \sim 2.3 \text{ years} \quad . \tag{15}$$

We assume further that total ozone abundance responds to altered NO abundance in a time much less than the various time lags between sunspot maxima and NO minima. From Figure 7, a best fit of Angell and Korshover's[18] compilation of ozone data gives t_L (Tromso) $\sim$ 2.7 years, in satisfactory agreement with the model calculation. For Arosa (ϑ = 47°) theory gives

$$t_L \text{ (Arosa)} - t_L \text{ (Tromso)} \sim 0.3 \text{ years} \quad , \tag{16}$$

compared with the published observational fit of 38 - 32 months = 0.5 years. The calculated amplitude at Arosa relative to Tromso of 0.6 is also close to the "observed" one. For equatorial regions the model suggests

$$t_L \text{ (equatorial)} - t_L \text{ (Tromso)} \sim 1.1 \text{ years} \quad , \tag{17}$$

compared with an observed lag of about 2.5 years. The computed amplitude in the tropics relative to that at high latitudes is about 0.2, perhaps about twice that observed. (Better fits to the time lags are obtained with a somewhat smaller horizontal diffusion coefficient K; the relative time lags for $\theta < \theta_o$ are proportional to $K^{-1/2}$.) The rough agreement with the Angell-Korshover analyses gives some additional support to the reality of the observed sunspot-ozone correlation and to cosmic-ray modulated NO in the high latitude regions as its origin. The quantitative agreement with relative amplitudes is somewhat fortuitous because of the varying NO altitude distributions at different latitudes (cf. Section VII).

VI ESTIMATES FOR ABSOLUTE MAGNITUDE OF COSMIC-RAY-INDUCED MODULATIONS OF OZONE

Over the polar regions ($\theta > 60°$) the calculated [NO] is given by Eq. (9) with Δ now replaced by t_L of Eq. (13). Then for the change in the column density, $\int [NO]\, dz$, we have

$$\Delta \int [NO]\, dz \sim 1 \times 10^{7} J_1 \cos [\omega(t - 2.5 \text{ years})] \quad , \quad \text{for } \theta > 60° \quad . \qquad (18)$$

From the magnitude and altitude dependence of cosmic-ray-modulated ionization of Figure 3, we obtain a column production of

$$J_1 \sim 8 \times 10^{6} \text{ molecules cm}^{-2} \text{ s}^{-1} \qquad (19)$$

and

$$\Delta \int [NO]\, dz \sim 8 \times 10^{13} \cos \omega(t - 2.5 \text{ years}) \text{ molecules cm}^{-2} \quad , \quad (\theta > 60°) \quad . \qquad (20)$$

The corresponding ozone variation measured at Tromso is about ±5 percent (cf., Figure 7).

A similar estimate follows for worldwide averages. The amplitude of the worldwide average of modulated NO, $\Delta \int \overline{[NO]}\, dz$, is independent of the horizontal diffusion; eliminating the K term from Eq. (5), we find

$$\Delta \int \overline{[NO]}\, dz = \frac{J_1 \cos(\omega t - \Phi)}{\left(\omega^2 + \tau^{-2}\right)^{1/2}} \frac{\pi r_o^2}{2\pi R_e^2} \quad , \tag{21}$$

with a mean phase lag of

$$\Phi = \tan^{-1} \omega\tau \quad . \tag{22}$$

Then

$$\Delta \int \overline{[NO]}\, dz \sim 4 \times 10^{13} \cos(\omega\tau - \Phi) \tag{23}$$

for $\tau \sim 3$ years.

The corresponding change in amplitude for the cyclic part of the world or Southern Hemisphere ozone-column density from Figure 8 is about 0.5 percent, consistent with a bigger effect from about a fivefold larger NO perturbation at Tromso (with a different altitude distribution). Appendix B summarizes arguments for a very rough dependence of

$$\frac{\Delta[O_3]}{[O_3]} \sim \frac{3}{8} \frac{\Delta[NO]}{[NO]} \tag{24}$$

in stratospheric models (e.g., Johnston,[23] and Chang and Duewer[24]), where ambient [NO] reduces ozone to about half what it would be from the Chapman cycle alone. Then, from Eqs. (20) and (23) and the corresponding observed ozone oscillations, the <u>ambient</u> NO column density would be

$$\int [NO]\, dz \sim \frac{3}{8} \times \frac{8 \times 10^{13}}{5 \times 10^{-2}} = 6 \times 10^{14} \frac{\text{molecule}}{\text{cm}^2} \quad , \tag{25}$$

corresponding to about 10^9 NO_x molecules cm^{-3} in the lower stratosphere or a relative concentration of about 1 ppb. This is lower but roughly

of the same order of magnitude as assumed in models in which NO contributes significantly to the control of ozone (cf. Figure 10, Chang and Duewer,[24] and Johnston et al.[20]). We emphasize that the estimate of Eq. (25) is extremely rough and can be taken only as support for the proposition that the computed cosmic-ray-modulated change in ozone has a reasonable magnitude.

Thus the magnitude as well as the time-lag and latitude-dependence of ozone variations seem consistent with the model for cosmic-ray-modulated NO as the origin of the 11-year cyclic ozone variation.

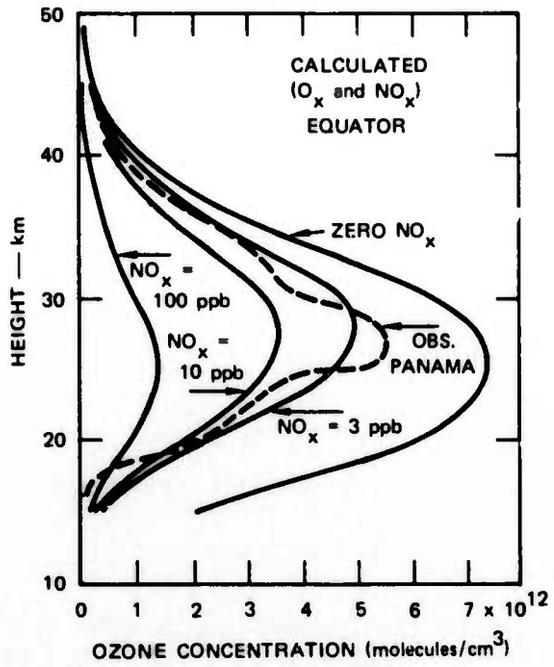

FIGURE 10 AN OZONE PROFILE OBSERVED AT PANAMA (9°N) COMPARED TO CALCULATED ONES FOR THE EQUATOR WITH NO_x MOLE FRACTIONS OF 3, 10, AND 100 ppb TO ACCOUNT FOR THE OZONE DEFICIT. Source: Ref. 23.

VII OZONE DEPRESSION FROM STRATOSPHERIC NO INJECTION BY ARTIFICIAL SOURCES

If the relation between sunspot activity and ozone suppression is real and caused by the calculated varying stratospheric NO injection, then existing ozone data can be used to predict suppression from other sources of NO.

A. Nuclear Explosions

Conventional analyses of expected NO stratospheric injection from nuclear explosions give 1 to 3 $\times$ 10^{34} NO molecules injected into the stratosphere during the 14-month period beginning August 1961 (Foley and Ruderman,[22] and Gilmore[7]). About 90 percent of the explosion yields were deposited at Novaya Zemla near the North Pole ($\theta = 72°$). The altitude distribution of this NO is presumably very similar to that of bomb-created C^{14}. Some distributions inferred from sampling data are given in Figures 11 through 16 (Telegdas[19]). It appears that C^{14} in the polar-cap region ($\theta > 60°$) has an initial distribution which peaks at around 18 km and a full width of about 10 km. This is qualitatively not very different from the computed altitude distribution of the modulated cosmic-ray-injected NO of Figure 3; therefore, the bomb-injected NO (assuming it follows bomb-injected C^{14}) may be expected to spread with an altitude distribution at each latitude similar to the distribution of NO from the 11-year oscillating polar source. That is, a direct comparison between the magnitudes of the ozone effects from the two different kinds of polar sources should be feasible.

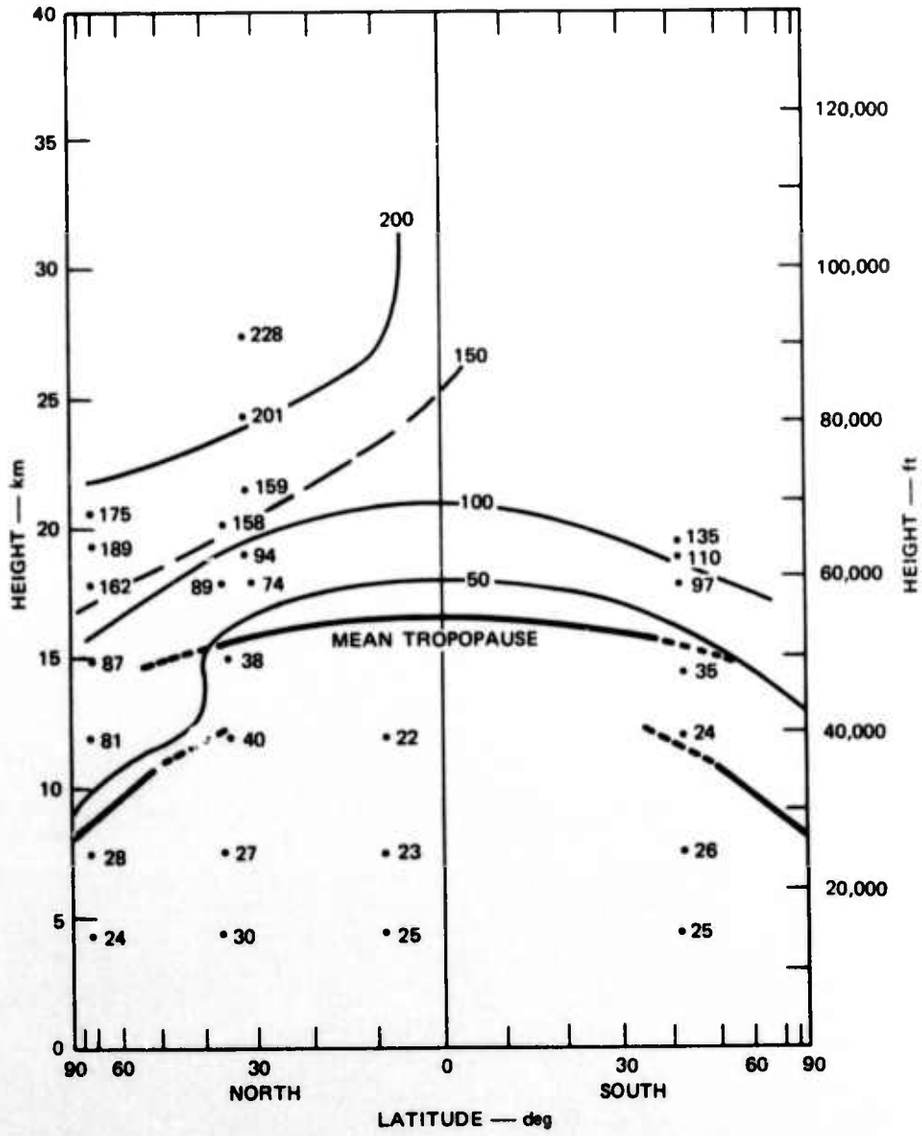

FIGURE 11 RESULTS OF ATMOSPHERIC C^{14} SAMPLING AND EXTRAPOLATION — MARCH-MAY, 1961 (Telegdas[19]). (The measured numbers and the isodensity line labels are in units of 10^5 C^{14} atoms per gram of air.)

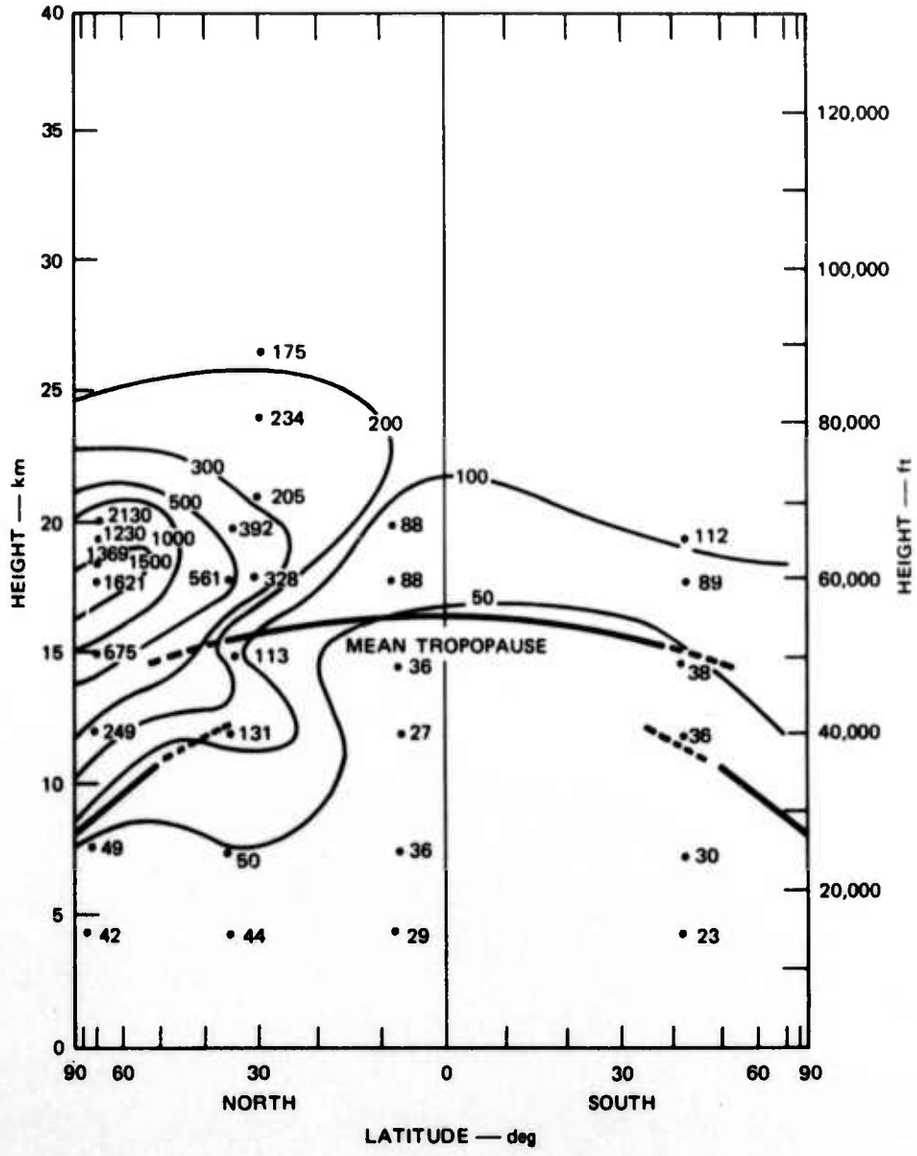

FIGURE 12 RESULTS OF ATMOSPHERIC C^{14} SAMPLING AND EXTRAPOLATION — MARCH-MAY 1962 (Telegdas[19]). (The measured numbers and the isodensity line labels are in units of 10^5 C^{14} atoms per gram of air.)

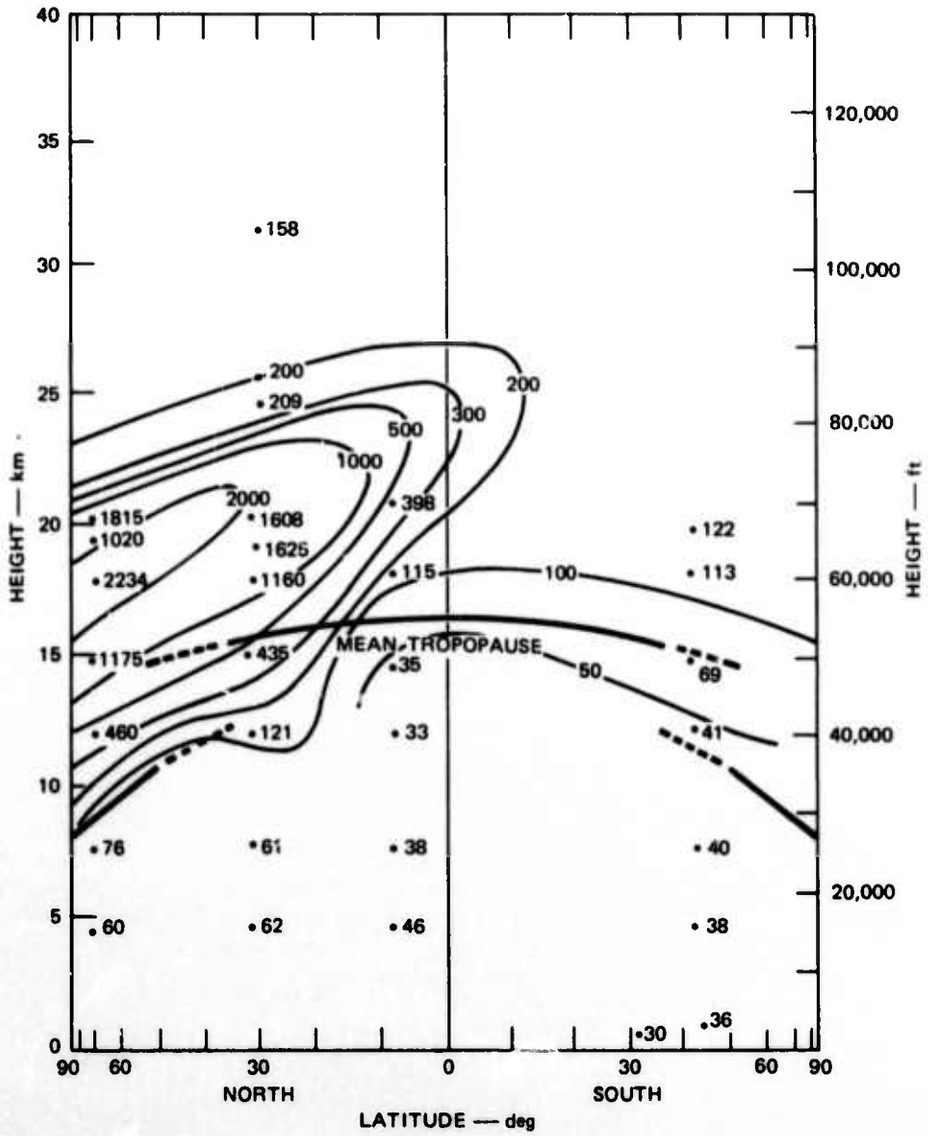

FIGURE 13 RESULTS OF ATMOSPHERIC C^{14} SAMPLING AND EXTRAPOLATION — DECEMBER 1962-FEBRUARY 1963 (Telegdas[19]). (The measured numbers and the isodensity line labels are in units of 10^5 C^{14} atoms per gram of air.)

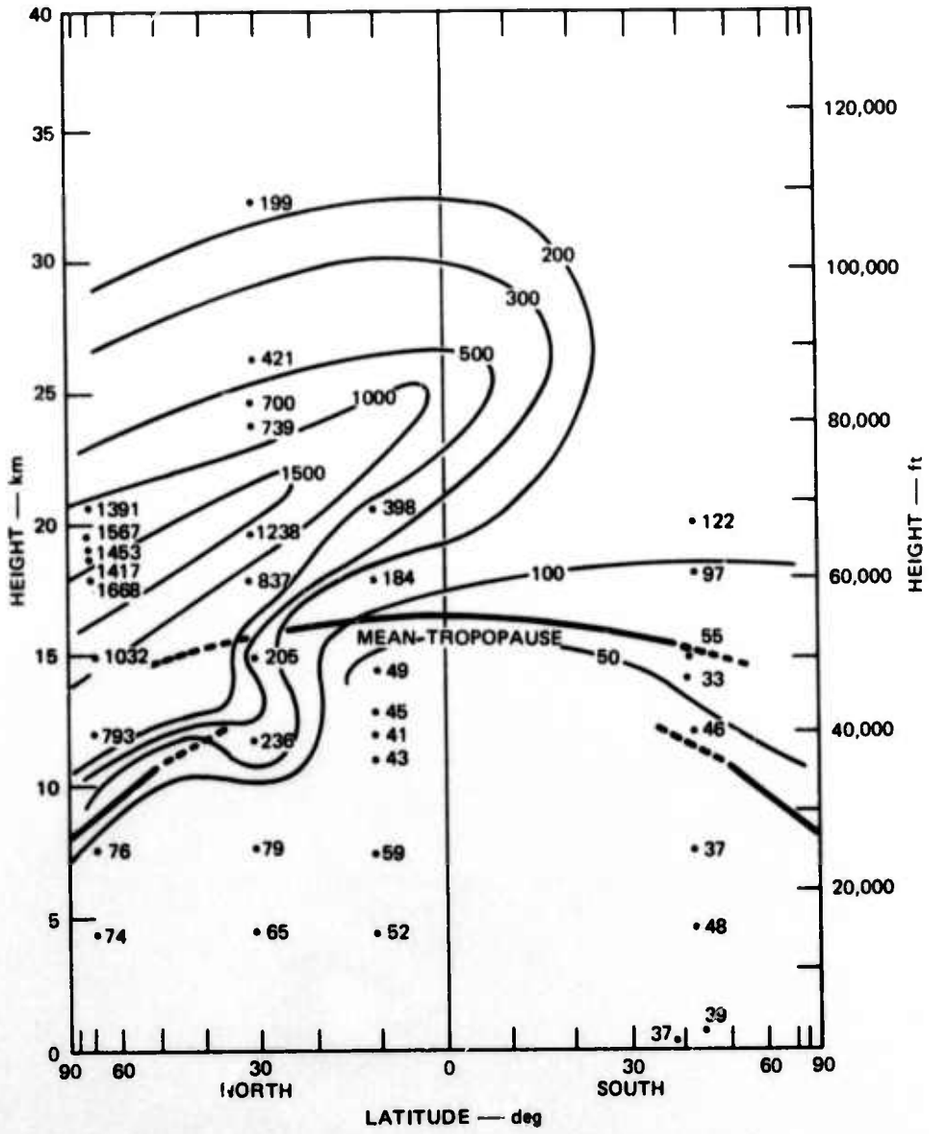

FIGURE 14 RESULTS OF ATMOSPHERIC C^{14} SAMPLING AND EXTRAPOLATION — MARCH-MAY 1963 (Telegdas[19]). (The measured numbers and the isodensity line labels are in units of 10^5 C^{14} atoms per gram of air.)

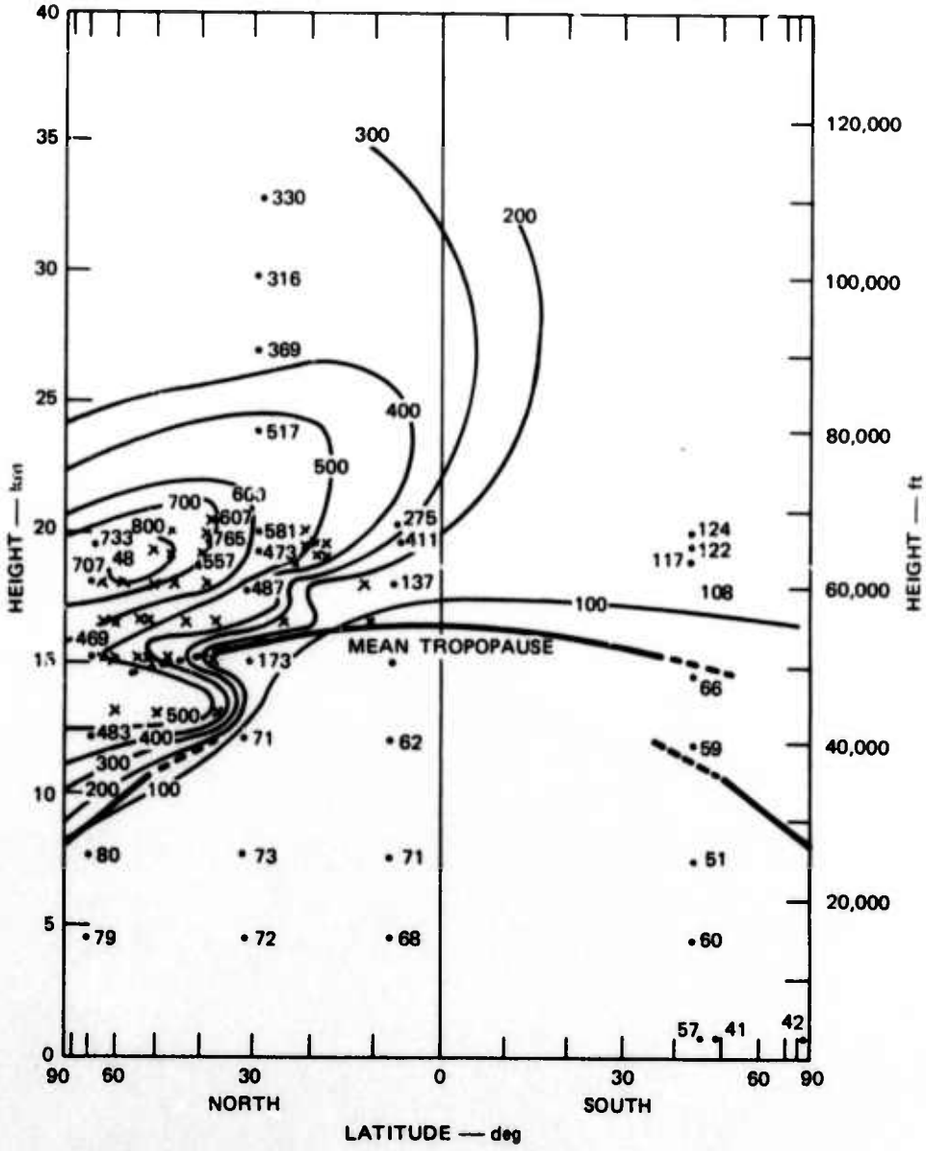

FIGURE 15 RESULTS OF ATMOSPHERIC C^{14} SAMPLING AND EXTRAPOLATION — MARCH-MAY 1964 (Telegdas[19]). (The measured numbers and the isodensity line labels are in units of 10^5 C^{14} atoms per gram of air.)

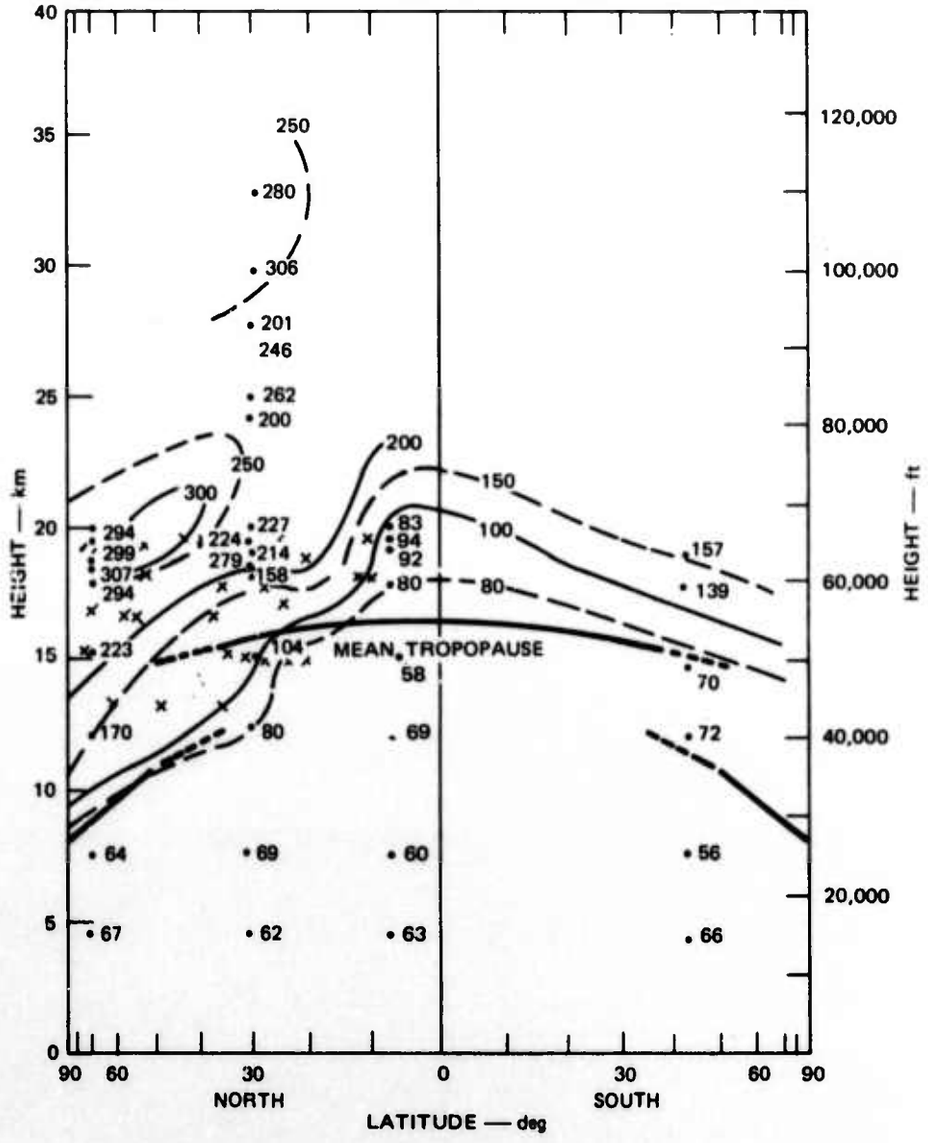

FIGURE 16 RESULTS OF ATMOSPHERIC C^{14} SAMPLING AND EXTRAPOLATION — MARCH-MAY 1966 (Telegdas[19]). (The measured numbers and the isodensity line labels are in units of 10^5 C^{14} atoms per gram of air.)

Johnston, Whitten, and Birks[20] have normalized bomb-injected NO to observed bomb-manufactured Sr^{90}. A similar analysis based upon bomb-manufactured C^{14} is given in Figure 9. A one megaton explosion produces 2×10^{16} C^{14} nuclei (within about 3×10^{4} cm of a low-altitude explosion). According to Gilmore the minimum NO production from the same explosion is about 4×10^{31} molecules. The radii of the respective volumes within which each species is made is comparable. Thus a reasonably conservative estimate suggests 2×10^{5} NO_x molecules per C^{14} atom. Figure 9 gives the total measured excess C^{14} burden of the stratosphere from bomb explosions. This peaks at 3.6×10^{28} C^{14}, implying 7×10^{33} NO in the first quarter of 1963. The 30-month running average for the Northern Hemisphere alone stays at near 2×10^{28} C^{14} nuclei from mid-1962 to the end of 1963, corresponding to perhaps 4×10^{33} NO atoms in the Northern Hemisphere stratosphere during this interval. Since there were about 5×10^{27} excess C^{14} atoms in the Northern Hemisphere stratosphere from previous tests before the intense testing of 1961-62, the extra NO inserted might conservatively be estimated as averaging at least 3×10^{33} NO during 1963. This gives an average column density of 1×10^{15} cm^{-2} with about the same altitude distribution as modulated NO from the cosmic rays. (This is less than the total minimum NO of 4×10^{15} obtained by averaging total produced NO because of losses from the stratosphere, 30-month averaging and perhaps imperfect injection.) The estimates of Section VI imply that a change in average NO column density of 10^{14} cm^{-2} produces a 1 to 2 percent change in ozone. The lower estimate together with the "minimum" NO bomb yield then suggest that 30-month running averages of total ozone should show a drop of 3 percent by mid-1961, continuing to a 10 percent depression by mid-1962, and remaining at that level until the end of 1963. From analyses of worldwide ozone data, Johnston, Whitten, and Birks[20] claim evidence for a world average ozone decrease of 3.3 percent during the 1960-62 interval of extensive testing. Such a decrease does

not appear in the analysis of Angell and Korshover[18] who find "little evidence of a reduction in total-ozone due to nuclear testing" down to less than a percent.

Therefore, if yields of the bomb NO into the stratosphere are as large as those estimated by Gilmore[7] and by Foley and Ruderman,[22] there seems to be a conflict with our proposed explanation of an 11-year ozone cycle and possibly also with ozone observations during and after the 1961-62 period of heavy testing. A much smaller amount of bomb-injected stratospheric NO_x in a form in which it catalyzes ozone destruction would be comforting to theories for NO suppression of ozone.

B. Supersonic Transports

If fleets of supersonic transports were to fly only at latitudes greater than 60° with the altitude distribution of Figure 3, then a comparison of the effects from the sources of Eqs. (20) and (23) with those of aircraft would involve no other additional assumptions except that the ozone response is linear with NO. The exhaust NO injected into the stratosphere would be expected to diffuse over the globe with the patterns and timing of Figures 11 through 16. Since $\tau \sim 2$ to 6 years is somewhat greater than the diffusion time from the pole to the equator ($\pi^2 R_e^2/16K \sim 1$ year) a steady source I (NO molecules s^{-1}), half in each polar cap, would raise stratospheric NO roughly uniformly by

$$\frac{I\tau}{4\pi R_e^2} \sim 4 \times 10^{14} \left(\frac{\tau}{2 \text{ years}}\right) I_{33} \frac{\text{NO molecules}}{\text{cm}^2} \qquad (26)$$

where I_{33} is the NO input from the SST fleet in units of 10^{33} molecules per year. A comparison with the effects of Eqs. (20) and (23) gives a predicted average worldwide suppression from an SST fleet at appropriate altitudes and latitudes, after a steady state is achieved, of

(4 to 8) $\left(\frac{\tau}{2 \text{ years}}\right) I_{33}$ percent, if the effect is small enough so that a linear extrapolation remains valid. Johnston[25] has estimated that 500 SST's flying seven hours per day would give $I_{33} \sim 30$, so that the corresponding effect on ozone would be very large. The SST flying altitude, near 20 km, is above most of the cosmic-ray-modulated NO insertion in the polar regions. However, the naturally varying source is well above the low polar tropopause, so postulating similar results at other latitudes, where much higher tropopauses will have NO sources just above them, may be reasonable in order to predict the effects of NO from SST flights.

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Appendix A

NO HEMISPHERICAL VARIATION FROM OSCILLATING POLAR SOURCES

In a plane with a spatially constant source $J_1 e^{i\omega t}$ within a circle of $r < r_o$ and zero source for $r > r_o$, the solution of Eq. (5) is

$$[NO] = e^{i\omega t}\left[\frac{J_1}{i\omega + \frac{1}{\tau}} + BI_o(z)\right] \tag{A-1}$$

for $r < r_o$, and

$$[NO] = e^{i\omega t}\left[AK_o(z)\right] \tag{A-2}$$

for $r > r_o$. In these equations

$$z^2 = \frac{r^2}{K}\left(i\omega + \frac{1}{\tau}\right) \tag{A-3}$$

$$A = \frac{J}{\left(i\omega + \frac{1}{\tau}\right) K_o\left(z_o\right)}\left[1 - \frac{K_o'\left(z_o\right) I_o\left(z_o\right)}{K_o\left(z_o\right) I_o'\left(z_o\right)}\right]^{-1} \tag{A-4}$$

and

$$B = A\,\frac{K_o'\left(z_o\right)}{I_o'\left(z_o\right)} \quad . \tag{A-5}$$

Here I_o and K_o are the usual modified Bessel functions and z_o is the value of z defined in Eq. (A-3) at the source radius $r = r_o$. We associate this radius with that of the polar cap for NO injection measured

along a meridian from the pole to latitude 60°. Then

$$r_o \sim 3.3 \times 10^8 \text{ cm} \quad . \tag{A-6}$$

Then with $\tau \sim 3$ years, we have

$$|z_o^2| \sim 0.5 \quad . \tag{A-7}$$

Within the cap and at $z = z_o$ we therefore keep only the first term in the expansion

$$I_o(z) = 1 + \frac{z^2}{4} + \mathcal{O}\left(\frac{z^2}{4}\right)^2 \quad . \tag{A-8}$$

Then the solutions (A-i) through (A-5) reduce to

$$[NO] = \frac{J_1 e^{i\omega t}}{\left(i\omega + \frac{1}{\tau}\right)} \frac{1}{(1 - \alpha)} \quad , \qquad z < z_o \tag{A-9}$$

$$[NO] = \frac{J_1 e^{i\omega t}}{\left(i\omega + \frac{1}{\tau}\right)(1 - \alpha)} \frac{K_o(z)}{K_o(z_o)} \quad , \qquad z > z_o \tag{A-10}$$

with

$$\alpha = \frac{K_o'(z_o) I_o(z_o)}{K_o(z_o) I_o'(z_o)} \quad . \tag{A-11}$$

Further approximations, valid in the limit $z_o \to 0$, are

$$I_o(z_o) \sim 1 \quad , \tag{A-12}$$

$$I_o'(z_o) \sim z_o/2 \quad , \tag{A-13}$$

$$K_o(z_o) \sim \left(-\ln z_o - \gamma + \ln 2\right) \quad , \tag{A-14}$$

and

$$K_1(z) \sim -\frac{1}{z_o} \quad , \tag{A-15}$$

where γ is the Euler constar 0.57721 .... From Eqs. (A-11) through (A-15)

$$\alpha \sim \frac{2}{z_o^2\left(\ln z_o + \gamma - \ln 2\right)} \quad . \tag{A-16}$$

Then

$$[NO] \sim \frac{J_1 e^{i\omega t} r_o^2}{2K}\left(-\gamma + \ln 2 - \ln z_o\right) \quad , \quad z < z_o \tag{A-17}$$

and

$$[NO] \sim \frac{J_1 e^{i\omega t} r_o^2}{2K}\left(-\gamma + \ln 2 - \ln z_o\right)\frac{K_o(z)}{K_o(z_o)} \quad , \quad z > z_o \quad . \tag{A-18}$$

When Eq. (A-3) for z_o is substituted into Eq. (A-17)

$$[NO] \sim \frac{J_1 e^{i\omega t} r_o^2}{2K}\left[0.11 - 0.5 \ln \frac{r_o^2}{K}\left(i\omega + \frac{1}{\tau}\right)\right] \tag{A-19}$$

$$z < z_o \ll 1 \quad .$$

With values for ω, τ (= 3 years), K, and r_o obtained from Eqs. (4), (3), (7), and (11) of the main text, we find

$$[NO] \sim 0.4 \frac{J_1 r_o^2}{K} \cos \omega\,(t - 1.3 \text{ years}) \equiv [NO]_o \quad , \quad z < z_o \quad . \tag{A-20}$$

For $z > z_o$ we use only the first term in the expansion

$$K_o(z) = \left(\frac{\pi}{2z}\right)^{1/2} e^{-z} \left\{1 - \frac{1}{8z} + \frac{9}{2(8z)^2} + \ldots\right\} \quad . \qquad \text{(A-21)}$$

Then Eq. (A-18) becomes

$$[NO] = [NO]_o\left(\frac{z_o}{z}\right)^{1/2} e^{-\left(z-z_o\right)} \quad , \quad z > z_o$$

$$= [NO]_o\left(\frac{\varphi_o}{\varphi}\right)^{1/2} \exp\left[-\left(\varphi - \varphi_o\right)R_e K^{-1/2}\left(\omega^2 + \tau^{-2}\right)^{1/4} e^{i\delta/2}\right] \quad , \qquad \text{(A-22)}$$

$$r > r_o$$

and

$$\delta \equiv \tan^{-1} \omega\tau \sim 1.0 \text{ rad} \qquad \text{(A-23)}$$

for $\tau \sim 3$ years and φ the radian angular distance from the pole. Numerical substitution gives

$$[NO] = [NO]_o\left(\frac{\varphi_o}{\varphi}\right)^{1/2} \exp\left[-\left(\varphi - \varphi_o\right)(1.1 + 0.62\ i)\right] \quad . \qquad \text{(A-24)}$$

Appendix B

OZONE VARIATION FROM CHANGE OF NO

In Section VI we relate the variation of [NO] to that in $[O_3]$. We can obtain a rough approximation for that relationship without a detailed knowledge of reaction rates, except to invoke the assumption that NO is necessary to account for lowering $[O_3]$ by a factor α below the ambient abundance indicated by pure-oxygen photochemistry.

Odd oxygen is governed by

$$\frac{d}{dt}\left([O] + [O_3]\right) = J - K_1[NO]\,[O] - K_2[O]\,[O_3] \quad , \qquad \text{(B-1)}$$

where J is the production rate of odd oxygen by photodissociation and

$$\frac{[O]}{[O_3]} = K_3 \quad . \qquad \text{(B-2)}$$

These relations yield

$$[O_3] = \frac{K_4}{\left(1 + K_5[NO]/[O_3]\right)^{1/2}} \quad . \qquad \text{(B-3)}$$

The factor α defined above means that, for the steady-state abundances of $[NO]_o$ and $[O_3]_o$,

$$K_5 \frac{[NO]_o}{[O_3]_o} = \alpha^2 - 1 \equiv \beta \quad . \qquad \text{(B-4)}$$

For a slightly perturbed $[O_3]$, we then have

$$[O_3] \approx \frac{K_4}{\left(1 + \beta[NO]/[NO]_o\right)^{1/2}} \quad , \qquad \text{(B-5)}$$

which leads directly to

$$\frac{\Delta[O_3]}{[O_3]} \approx - \frac{\left(\alpha^2 - 1\right)}{2\alpha^2} \frac{\Delta[NO]}{[NO]_o} \quad , \qquad \text{(B-6)}$$

where it is implicitly assumed that $\Delta[NO]$ has a similar altitude dependence to $[NO]_o$. Although crude in its derivation, the equation above seems to be an adequate "rule of thumb." For $\alpha \sim 2$, it agrees reasonably with more detailed model calculations by Johnston[23] summarized in Figure 10 and by Chang and Duewer.[24]

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